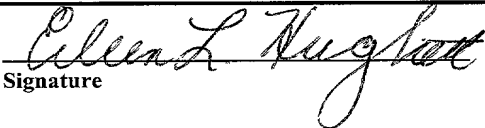


404 Rec'd PCT/PTO 16 OCT 1998

FORM PTO-1390 OFFICE (Rev. 10-95)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK		ATTORNEY'S DOCKET NUMBER	
<b>TRANSMITTAL LETTER TO THE UNITED STATES          DESIGNATED/ELECTED OFFICE (DO/EO/US)          CONCERNING A FILING UNDER 35 U.S.C. 371</b>				6065 U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/171377	
INTERNATIONAL APPLICATION NO. PCT/US97/06484		INTERNATIONAL FILING DATE 16 April 1997		PRIORITY DATE CLAIMED 17 April 1996	
TITLE OF INVENTION <b>High Density Detergent-Making Process Using A High Active Surfactant Paste Having Improved Stability</b>					
APPLICANT(S) FOR DO/EO/US <b>BOHLEN, David Scott; JENSEN, Michael Chris; HOLLIHAN, Lester John; ;</b>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.					
1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application was filed (35 U.S.C. 371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11. to 16. below concern document(s) or information included: 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input checked="" type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information:					
"Express Mail" mailing label number <u>EM032707360US</u> Date of Deposit <u>16 Oct. 1997</u> I hereby certify that this paper/fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231 Donna L. Butts Administrator Mailing Application Signature					

09/171377

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO. PCT/US97/06484		ATTORNEY'S DOCKET NUMBER 6065	
				CALCULATIONS    PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$720	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	10-20 =	0	x \$22.00	\$0	
Independent Claims	1-3 =	0	x \$78.00	\$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			\$250.00	\$0	
TOTAL OF ABOVE CALCULATIONS =				\$720	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0	
TOTAL NATIONAL FEE =				\$720	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +				\$0	
TOTAL FEES ENCLOSED =				\$720	
				Amount to be refunded	\$
				charged	\$
<p>a. <input type="checkbox"/> A check in the amount of \$ ____ to cover the above fees is enclosed.</p> <p>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>16-2480</u> in the amount of \$ <u>720</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>16-2480</u>. A duplicate copy of this sheet is enclosed.</p> <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO:</p>					
K.K. Patel, Patent Attorney Patent Division The Procter & Gamble Company Ivorydale Technical Center 5299 Spring Grove Avenue Cincinnati, OH 45217				<div style="text-align: center;">             Signature         </div> <div style="text-align: center;">           Eileen L. Hughett            Name         </div> <div style="text-align: center;"> <u>34,352</u>            Registration Number         </div>	

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09/171377

Case 6065

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of

U.S. National Phase Entry  
Under 35 USC 371 from  
the International Application of  
BOHLEN, David Scott et al  
Int'l Application No. PCT/US97/06484  
Filed in the RO/US on 16 April 1997  
Entitled: *High Density Detergent-Making Process  
Using A High Active Surfactant Paste  
Having Improved Stability*

"Express Mail" mailing label number: EW03270736045  
Date of Deposit: 16 October 1998  
I hereby certify that this paper and/or fee is being  
deposited with the United States Postal Service "Express  
Mail Post Office to Addressee" service under 37 CFR 1.10  
on the date indicated above and is addressed to the  
Commissioner for Patents and Trademarks, Washington,  
D.C. 20231.  
Name: Donna L. Butts  
Signature: Donna L. Butts

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

Dear Sir:

Before computing the fees for entering the captioned International Application into the U.S. National Phase, please enter the following amendments **IN THE CLAIMS**:

- \* In Claim 1 please replace the phrase "characterized by" with --comprising--.
- \* In Claim 3 please replace the phrase "claims 1-2" with --Claim 1--.
- \* In Claim 4 please replace the phrase "claims 1-3" with --Claim 1--.
- \* In Claim 5 please replace the phrase "claims 1-4" with --Claim 1--. Also, please replace the phrase "characterized by" with --comprising--.
- \* In Claim 6 please replace the phrase "claims 1-5" with --Claim 1--.
- \* In Claim 7 please replace the phrase "claims 1-6" with --Claim 1--.
- \* In Claim 8 please replace the phrase "claims 1-7" with --Claim 1--.
- \* In Claim 9 please replace the phrase "claims 1-8" with --Claim 1--.
- \* In Claim 10 please replace the phrase "claims 1-9" with --Claim 1--. Also, please replace the phrase "characterized by" with --comprising--.

Please add the following new claims:

11. A process for preparing detergent agglomerates comprising the steps of:
  - (a) providing a non-linear viscoelastic surfactant paste including, by weight of said surfactant paste, from about 70% to 80% of a mixture of C<sub>14-15</sub> alkyl sulfate surfactant and C<sub>12-13</sub> linear alkylbenzene sulfonate surfactant, from about 15% to about 20% of water, from about 2% to about 8% of polyethylene glycol and from about 0.5% to about 1% of sodium hydroxide such that the pH of said surfactant paste is at least about 11;

09 OCT 1998

- (b) regulating the temperature of said surfactant paste within a range from about 65°C to about 70°C so that said surfactant paste is processable and stable for at least 120 hours;
- (c) charging from about 25% to about 65% by weight of said surfactant paste into a high speed mixer/densifier;
- (d) inputting from about 1% to about 70% by weight of a detergency builder into said high speed mixer/densifier;
- (e) agglomerating said surfactant paste and said builder by treating said surfactant paste and said builder initially in said high speed mixer/densifier and subsequently in a moderate speed mixer/densifier to form said detergent agglomerates; and
- (f) drying said detergent agglomerates.

12. The process of claim 11 wherein said surfactant paste is substantially free of materials which produces a gas when reacted with an acid.

13. The process of claim 11 wherein said alkyl sulfate surfactant and said linear alkylbenzene sulfonate surfactant are included in said surfactant paste in a weight ratio of about 3:1.

14. The process of claim 11 further comprising the step of maintaining said surfactant paste substantially free of contaminant materials having a pH of less than about 7.

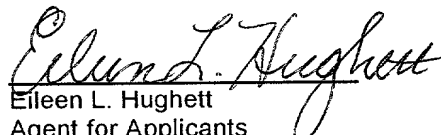
15. A detergent composition comprising detergent agglomerates made according to the process of claim 1.

16. A detergent composition comprising detergent agglomerates made according to the process of claim 11.

The support for these amendments is found in the claims as originally filed. These amendments are being entered to bring the claims into conformance with, *inter alia*, 37 CFR §1.75; no new matter is added.

Respectfully submitted for Applicants,

By:

  
Eileen L. Hughett  
Agent for Applicants  
Registration No. 34,352

15 October 1998  
5299 Spring Grove Avenue  
Cincinnati, Ohio 45217-1087  
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TDR:jmh

28 Rec'd -CT/PTC 18 OCT 1998

**HIGH DENSITY DETERGENT-MAKING PROCESS USING A HIGH ACTIVE  
SURFACTANT PASTE HAVING IMPROVED STABILITY**

5

**FIELD OF THE INVENTION**

The present invention is generally directed to a process for making high density  
10 detergent compositions from a high active surfactant paste and other detergent ingredients.  
More particularly, the invention is directed to a process for producing a high density  
detergent composition in the form of agglomerates in which the stability and shelf life of a  
high active surfactant paste is unexpectedly improved and maintained. This process is  
especially useful in the production of modern compact granular detergent compositions  
15 which typically require higher levels of active deterative surfactants.

**BACKGROUND OF THE INVENTION**

Recently, there has been considerable interest within the detergent industry for  
laundry detergents which are "compact" and therefore, have low dosage volumes. To  
facilitate production of these so-called low dosage detergents, many attempts have been  
20 made to produce high bulk density detergents, for example with a density of 650 g/l or  
higher. The low dosage detergents are currently in high demand as they conserve resources  
and can be sold in small packages which are more convenient for consumers.

Generally, there are two primary types of processes by which detergent granules or  
powders can be prepared. The first type of process involves spray-drying an aqueous  
25 detergent slurry in a spray-drying tower to produce highly porous detergent granules. In  
the second type of process, various detergent components are mixed after which they are  
agglomerated with a nonionic or anionic detergent paste that also serves as the binder for  
the agglomerated particle itself. In both processes, the most important factors which  
govern the density of the resulting detergent granules are the density, porosity and surface  
30 area of the various starting materials and their respective chemical composition. These  
parameters, however, can only be varied within a limited range. Thus, a substantial bulk  
density increase can only be achieved by additional processing steps which lead to  
densification of the detergent granules or via build-up agglomeration processes.

The art is replete with processes directed to agglomeration for producing detergent  
35 compositions. For example, attempts have been made to agglomerate detergent builders by  
mixing zeolite and/or layered silicates in a mixer to form free flowing agglomerates. Yet  
another example involves a starting detergent material in the form of highly active,

viscoelastic surfactant paste which is agglomerated with dry powders such as aluminosilicates and carbonates into crisp, free flowing, highly dense detergent agglomerates. However, a wide variety of problems have been encountered with handling high active, highly viscoelastic surfactant pastes which are used to produce high density, high active detergent agglomerates suitable for modern low dosage detergent products. Specifically, such high active surfactant pastes are extremely sensitive to environmental and operating equipment parameters, all of which make the pastes difficult to transport, store and process when producing detergent agglomerates.

Typically, surfactant pastes are manufactured by a process in which fatty alcohol is sulfated, and thereafter, neutralized with an alkaline material (e.g. sodium hydroxide). This is an extremely delicate process, especially when used to produce high active surfactant pastes predominantly (greater than 60% by weight) containing the active surfactant and only a relatively minor amount of water and adjuncts. The resulting high active surfactant pastes are extremely sensitive to their environment, for example., high temperature zones or "hot spots" in the equipment (pipes, valves, storage tanks and the like) to which it is exposed as well as any contaminants having a pH of less than 7 which make their way into the paste. In the event that the high active surfactant paste is exposed to one or more of these environmental factors, such high active pastes have a tendency to undergo a hydrolysis reaction, wherein the surfactant reverts back to its alcohol form. This hydrolysis reaction is an autocatalytic reaction in that a by-product is an acid which continues to react with any remaining surfactant. This threat of hydrolysis particularly exacerbates the environmental sensitivity of high surfactant pastes and renders them difficult to keep stable over periods of time (e.g. 2-7 days) necessary for large-scale commercial manufacture of modern compact laundry detergents. It should be understood that even hydrolysis of 1% by weight of the surfactant paste can have major financial consequences in large-scale commercial manufacturing of detergent products.

Typical prior art attempts in this area involved immediately forming surfactant particles after the paste was manufactured. However, this requires "on-site" particle forming equipment or requires the surfactant-making equipment to be housed in or near the detergent manufacturing facility. Currently, detergent-making and surfactant paste-making industries have become separated both physically as well as from a commercial standpoint, a trend which is only increasing. Thus, it would be desirable to have a high active surfactant paste which remains stable over longer periods of time so as to enable the surfactant-making operation to be located farther away from the detergent-making facility which is more representative of the current commercial environment.

Yet another challenge with the use of such high active surfactant pastes involves their rheological properties in that they must have a low enough viscosity to be pumped in

and out of transport trucks or trains and in and out of storage tanks at the detergent manufacturing facility. Any significant temperature changes may lead to undesirable gelling or solidification of the surfactant paste causing increases in manufacturing expenses and time. Note, however, that different rheological properties of the surfactant paste may  
5 result upon reheating.

Also in that regard, additional ingredients such as carbonates which are included so as to maintain the storage and transport stability of the surfactant paste before it is processed has the effect of increasing the viscoelasticity of the high active surfactant paste, therefore rendering it very difficult to process. The difficulty in processing arises due to a  
10 change in the viscoelasticity of the surfactant paste which requires relatively expensive high-pressure pumps, larger pipe lines and shorter transport distances to be implemented into the detergent-making process. As a consequence, it would be desirable to have a process in which the storage stability of the paste is maintained without sacrificing its processability.

Accordingly, despite the above-mentioned disclosures in the art, there remains a need for a process for producing an agglomerated detergent composition from a high active surfactant paste which is sufficiently stable during transportation and storage for sufficient periods of time so as to enable large-scale commercial manufacture of modern compact detergent compositions. Also, there remains a need for such a process which is inexpensive  
15 and can be easily incorporated into large-scale production facilities for low dosage or compact detergents.  
20

#### BACKGROUND ART

The following references are directed to surfactant pastes: Aouad et al, WO 93/18123 (Procter & Gamble); Aouad et al, WO 92/18602 (Procter & Gamble); Aouad et  
25 al, EP 508,543 (Procter & Gamble); Mueller et al, U.S. Patent no. 5,152,932; Strauss et al, U.S. Patent No. 5,080,848 (Procter & Gamble); Ofosu-Asante et al, U.S. Patent No. 5,066,425 (Procter & Gamble); Jolicoeur et al, U.S. Patent No. 5,045,238 (Procter & Gamble); and Van Zorn et al, EP 504,986 (Shell). The following references are directed to densifying spray-dried granules: Appel et al, U.S. Patent No. 5,133,924 (Lever); Bortolotti  
30 et al, U.S. Patent No. 5,160,657 (Lever); Johnson et al, British patent No. 1,517,713 (Unilever); and Curtis, European Patent Application 451,894. The following references are directed to producing detergents by agglomeration: Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble); Capeci et al, U.S. Patent No. 5,366,652 (Procter & Gamble); Capeci et al, U.S. Patent No. 5,486,303 (Procter & Gamble); Capeci et al, U.S. Patent No. 5,489,392  
35 (Procter & Gamble); Hollingsworth et al, European Patent Application 351,937 (Unilever); and Swatling et al, U.S. Patent No. 5,205,958.

#### SUMMARY OF THE INVENTION

The present invention meets the needs identified above by providing a process for making detergent agglomerates from a high active surfactant paste and a detergent builder. There is a significant advantage with this process in that the surfactant paste is stable, pumpable, and transportable over an extended period of time so as to facilitate multi-  
5 location, large-scale manufacture of modern compact detergent products. In particular, the high active surfactant paste can be manufactured in one facility, and thereafter, stored and transported to a remote facility for further processing into the finished detergent agglomerates.

As used herein, the term "contaminants" means any foreign substance with which  
10 the surfactant paste comes into contact while being stored and transported prior to the inputting and agglomerating steps in the process. Examples of such contaminants include, but are not limited to, multi-colored residue of sulfuric acid, sodium sulfate, fatty alcohol, iron, chromium, and nickel. As used herein with respect to the surfactant paste, the term "stable" means that the surfactant paste substantially retains its formulation which contains  
15 a neutralized surfactant and has not significantly reverted via hydrolysis back to its alcohol form. As used herein with respect to the surfactant paste, the term "processable" means that the surfactant paste retains desirable rheological properties so as to allow it to be used in the current process which typically means that it will have a viscosity as detailed hereinafter with respect to the Power Law Model. As used herein, the term "agglomerates"  
20 refers to particles formed by agglomerating detergent granules or particles which typically have a smaller mean particle size than the formed agglomerates. All percentages and ratios used herein are expressed as percentages by weight (anhydrous basis) unless otherwise indicated. All documents are incorporated herein by reference. All viscosities referenced herein are measured at 70°C ( $\pm 5^\circ\text{C}$ ) and at shear rates of about 10 to 100  $\text{sec}^{-1}$  unless  
25 indicated otherwise.

In accordance with one aspect of the invention, a process for producing detergent agglomerates is provided. The process comprises the steps of: (a) providing a non-linear viscoelastic surfactant paste including, by weight of the surfactant paste, from about 70% to 95% of a deterative surfactant, from about 5% to about 30% of water, and an excess amount  
30 of an alkali metal hydroxide such that the pH of the surfactant paste is at least about 10; (b) regulating the temperature of the surfactant paste within a range from about 50°C to about 80°C so that the surfactant paste is processable and stable for at least 48 hours; (c) charging the surfactant paste into a high speed mixer/densifier; (d) inputting from about 1% to about 70% by weight of a detergency builder into the high speed mixer/densifier; and (e)  
35 agglomerating the surfactant paste and the builder by treating the surfactant paste and the builder initially in the high speed mixer/densifier and subsequently in a moderate speed mixer/densifier so as to form the detergent agglomerates.



In accordance with a highly preferred aspect of the invention, another process for producing detergent agglomerates is provided. The process comprises the steps of: (a) providing a non-linear viscoelastic surfactant paste including, by weight of the surfactant paste, from about 70% to 80% of a mixture of C<sub>14-15</sub> alkyl sulfate surfactant and C<sub>12-13</sub> linear alkylbenzene sulfonate surfactant, from about 15% to about 20% of water, from about 2% to about 8% of polyethylene glycol and from about 0.5% to about 1% of sodium hydroxide such that the pH of the surfactant paste is at least about 11; (b) regulating the temperature of the surfactant paste within a range from about 65°C to about 70°C so that the surfactant paste is processable and stable for at least 120 hours; (c) charging from about 1% to about 50% by weight of the surfactant paste into a high speed mixer/densifier; (d) inputting from about 1% to about 70% by weight of a detergency builder into the high speed mixer/densifier; (e) agglomerating the surfactant paste and the builder by treating the surfactant paste and the builder initially in the high speed mixer/densifier and subsequently in a moderate speed mixer/densifier to form the detergent agglomerates; and (f) drying the detergent agglomerates. The present invention also provided detergent compositions comprising detergent agglomerates made in accordance with any of the processes described herein.

Accordingly, it is an object of the invention to provide a process for producing an agglomerated detergent composition from a high active surfactant paste which is sufficiently stable during transportation and storage for sufficiently extended periods of time so as to enable large-scale commercial manufacture of modern compact detergent compositions. It is also an object of the invention to provide such a process which is inexpensive and can be easily incorporated into large-scale production facilities for low dosage or compact detergents. These and other objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following detailed description of the preferred embodiment and the appended claims.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Generally, the present process is used in the production of low dosage detergents, whereby the resulting detergent agglomerates can be used as a detergent or as a detergent additive. In particular, the process can be used to form "high active" (i.e. high surfactant level) detergent agglomerates which are used as an admix for purposes of enhancing the active levels in granular low dosage detergents, and thereby, allow for more compact detergents.

#### Process

The process produces free flowing, high density detergent agglomerates, preferably having a density of at least 650 g/l. The process produces high density detergent agglomerates from a highly active and viscoelastic surfactant paste having a relatively low

water content. In the past, processing and storing certain highly viscoelastic, high active surfactant pastes has been a problem, especially in light of their sensitivity to temperature variations and contaminants which are acidic in nature. While not intending to be bound by theory, it is believed that such temperature variations and acidic contaminants cause the autocatalytic hydrolysis reaction of the surfactant paste which effectively reverts the surfactant paste to an aqueous alcohol solution that cannot be reprocessed. It has therefore been found that optimally selected temperature ranges and pH ranges of contaminants must be regulated in order to produce the desired detergent agglomerates which are used in modern compact detergent products.

In the first step of the process, a non-linear viscoelastic surfactant paste is provided which is characteristic of many highly active, highly viscoelastic pastes used in producing high density detergent agglomerates. The phrase "nonlinear viscoelastic" means that the paste has a nonlinear fluid velocity profile and exhibits viscoelastic fluid behavior, i.e. it can be stretched during flow such as chewing gum or the like. Until now, such nonlinear viscoelastic surfactant pastes have been very difficult to process and keep stable. Preferably, the surfactant paste comprises, by weight of the surfactant paste, from about 70% to about 95%, more preferably from about 70% to about 85%, and most preferably from about 70% to about 75%, of a deterative surfactant.

In a preferred embodiment, the surfactant paste is a mixture of C<sub>14-15</sub> alkyl sulfate ("AS") and C<sub>12-13</sub> linear alkylbenzene sulfonate ("LAS") surfactants in a weight ratio of from about 1:1 to about 5:1 (AS:LAS). Another preferred embodiment herein contemplates a surfactant paste mixture having a weight ratio of C<sub>14-15</sub> alkyl sulfate to C<sub>12-13</sub> linear alkylbenzene sulfonate of about 3:1. Other optional surfactant systems include pure AS or pure LAS surfactants in the paste as well as alkyl ethoxy sulfate ("AES") systems in which AES is the sole or one of the surfactants in the paste.

The surfactant paste also includes from about 5% to about 30%, more preferably from about 15% to about 25%, and most preferably from about 15% to about 20%, by weight of the paste, of water. Additionally, the paste includes from about 0.1% to about 10%, more preferably from about 1% to about 8%, and most preferably from about 2% to about 8%, by weight of the paste, of polyethylene glycol. The surfactant paste also contains from about 0.01% to about 5%, more preferably from about 0.1% to about 1%, and most preferably from about 0.5% to about 1%, by weight of the paste, of an alkali metal hydroxide which preferably is sodium hydroxide. Also included in the surfactant paste are minor ingredients such as unreacted alcohols, sulfates and the like, although it is preferable to keep these amounts to a minimum.

In the subsequent step of the process, the surfactant paste is regulated within a temperature range of from about 50°C to about 80°C, more preferably from about 60°C to

about 75°C, and most preferably from about 65°C to about 70°C. Preferably, the regulating step maintains or renders the surfactant paste stable for at least 48 hours, more preferably for at least 72 hours, and most preferably for at least 170 hours. In this way, the likelihood of the surfactant paste undergoing the undesirable hydrolysis reaction and/or being difficult to transport and process due to unbearable rheological properties, such as high viscosity, is eliminated.

Furthermore, it is preferable that the surfactant paste be substantially free of materials which produces a gas when reacted with an acid. Such materials include carbonates, percarbonates, perborates or any other material which produces a gas upon contact with an acidic material. While not intending to be bound by theory, it is hypothesized that if the surfactant paste includes such a gas-producing material, it will react with any acidic contaminant material to produce a gas that propagates through the remaining surfactant paste, thereby creating a "channel" or "path" through which the acidic contaminant can traverse the paste. This facilitates the hydrolysis reaction of the entire surfactant paste as opposed to only a small isolated hydrolysis incident which would not otherwise affect the overall surfactant paste composition. Also in this regard, it is preferable in the current process to maintain the surfactant paste substantially free of contaminant materials having a pH of less than about 7.

In the next step of the process, the surfactant paste is charged into a high speed mixer/densifier (e.g. Lödige Recycler CB 30) which typically operates in 300 rpm to about 2500 rpm range. In this step, from about 25% to about 65%, more preferably 30% to about 60%, and most preferably from about 35% to about 55%, by weight of the surfactant paste, is used in the process to make the agglomerates. Also, from about 1% to about 70%, more preferably from about 5% to about 70% and, most preferably from about 50% to about 70%, by weight of a detergency builder is inputted into the high speed mixer/densifier. Although other builders can be used in the process as described hereinafter, aluminosilicate builder is the preferred.

The surfactant paste and the builder are agglomerated by treating the paste and the builder initially in the high speed mixer/densifier and subsequently in a moderate speed mixer/densifier (e.g. Lödige Recycler KM 300 "Ploughshare" having a large central shaft operating in the 100 rpm to 300 rpm range) so as to form detergent agglomerates. Other equipment suitable for use as the high speed mixer/densifier or moderate speed mixer/densifier are described in Capeci, U.S. Patent 5,366,652, the disclosure of which is incorporated herein by reference. Optionally, other conventional detergent ingredients as described hereinafter can also be inputted into the high speed mixer/densifier and/or moderate speed mixer/densifier to make a fully formulated detergent agglomerate.

5 The surfactant paste, builder and other optional starting detergent materials are sent to a moderate speed mixer/densifier for further build-up agglomeration resulting in agglomerates having a density of at least 650 g/l and, more preferably from about 700 g/l to about 900 g/l. Preferably, the mean residence time of the surfactant paste and other starting detergent materials in the high speed mixer/densifier (e.g. Lödige Recycler CB 30 mixer/densifier) is from about 1 to 30 seconds while the residence time in low or moderate speed mixer/densifier (e.g. Lödige Recycler KM 300 "Ploughshare" mixer/densifier) is from about 0.25 to 10 minutes.

10 Inevitably, a certain amount of the agglomerates exiting the moderate speed mixer/densifier will be below the predetermined particle size range and optionally, can be separated and recycled back to the high speed mixer/densifier for further build-up agglomeration. In that regard, these so-called undersized agglomerates or "fines" will comprise from about 5% to about 30% by weight of the detergent agglomerates.

15 The particle porosity of the resulting detergent agglomerates produced according to the process of the invention is preferably in a range from about 5% to about 20%, more preferably at about 10%. The combination of the above-referenced porosity and particle size results in agglomerates having density values of 650 g/l and higher. Such a feature is especially useful in the production of low dosage laundry detergents as well as other granular compositions such as dishwashing compositions.

20 The process can comprise the steps of spraying an additional binder in the mixer/densifier(s) used in the agglomeration step to facilitate production of the desired detergent agglomerates. A binder is added for purposes of enhancing agglomeration by providing a "binding" or "sticking" agent for the detergent components. The binder is preferably selected from the group consisting of water, anionic surfactants, nonionic surfactants, polyethylene glycol, polyacrylates, citric acid and mixtures thereof. Other suitable binder materials including those listed herein are described in Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble Co.), the disclosure of which is incorporated herein by reference.

30 Another optional step contemplated by the present process includes conditioning the detergent agglomerates by drying the detergent agglomerates after the moderate speed mixer/densifier. Yet another optional step involves adding a coating agent (e.g. aluminosilicates, carbonates, sulfates, or any other dry powdered material) to the detergent agglomerate before or after they exit the moderate speed mixer/densifier for purposes of enhancing the flowability of the agglomerates (i.e. reduce caking). This further enhances the condition of the detergent agglomerates for use as an additive or to place them in shippable or packagable form. Those skilled in the art will appreciate that a wide variety of methods may be used to dry as well as cool the exiting detergent agglomerates without

departing from the scope of the invention. By way of example, apparatus such as a fluidized bed can be used for drying while an airlift can be used for cooling should it be necessary.

#### Surfactant Paste

5           The viscoelastic surfactant paste used herein has viscoelastic fluid properties which can be described by a commonly used mathematical model that accounts for the shear thinning nature of the paste. The mathematical model is called the Power Law Model and is described by the following relation:

$$\sigma = K\gamma^n$$

10       where  $\sigma$  = Shear Stress (dynes/cm<sup>2</sup>),  $K$  = Consistency (Poise·sec<sup>n-1</sup>),  $\gamma$  = Shear Rate (sec<sup>-1</sup>), and  $n$  = Rate Index (dimensionless). The rate index  $n$  varies from 0 to 1. The closer  $n$  is to 0, the more shear thinning the fluid. The closer  $n$  is to 1, the closer it is to simple Newtonian behavior, i.e. constant viscosity behavior.  $K$  can be interpreted as the apparent viscosity at a shear rate of 1 sec<sup>-1</sup>.

15           In this context, the viscoelastic surfactant paste used in the process has a consistency  $K$  at 70°C of from about 50,000 to about 250,000 cPoise·sec<sup>n-1</sup> (500 to 2,500 Poise·sec<sup>n-1</sup>), more preferably from about 100,000 to about 195,000 cPoise·sec<sup>n-1</sup> (1,000 to 1,950 Poise·sec<sup>n-1</sup>), and most preferably from about 120,000 to about 180,000 cPoise·sec<sup>n-1</sup> (1,200 to 1,800 Poise·sec<sup>n-1</sup>). Preferably, the surfactant paste has a shear index  $n$  of from about 0.05 to about 0.25, more  
20       preferably from about 0.08 to about 0.20 and most preferably from about 0.10 to about 0.15.

          The surfactant in the paste can be selected from anionic, nonionic, zwitterionic, ampholytic and cationic classes and compatible mixtures thereof. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, both of which are  
25       incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both of which are also incorporated herein by reference. Of the surfactants, anionics and nonionic are preferred and anionics are most preferred.

30           The following are representative examples of detergent surfactants useful in the present surfactant paste. Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about  
35       18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of

the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional anionic surfactants which suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ( $C_{8-18}$  carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as  $C_{11-13}$  LAS.

Other anionic surfactants suitable for use herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

In addition, suitable anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred anionic surfactants are  $C_{10-18}$  linear alkylbenzene sulfonate and  $C_{10-18}$  alkyl sulfate. If desired, low moisture (less than about 25% water) alkyl sulfate paste can be the sole ingredient in the surfactant paste. Most preferred are  $C_{10-18}$  alkyl sulfates, linear or branched, and any of primary, secondary or tertiary. A preferred embodiment of the present invention is wherein the surfactant paste comprises from about 20% to about

40% of a mixture of sodium C<sub>10-13</sub> linear alkylbenzene sulfonate and sodium C<sub>12-16</sub> alkyl sulfate in a weight ratio of about 2:1 to 1:2. Another preferred embodiment of the detergent composition includes a mixture of C<sub>10-18</sub> alkyl sulfate and C<sub>10-18</sub> alkyl ethoxy sulfate in a weight ratio of about 80:20.

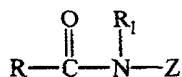
5 Water-soluble nonionic surfactants are also useful in the instant invention. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a  
10 water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration,  
15 with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol. Included are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

An additional group of nonionics suitable for use herein are semi-polar nonionic  
20 surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing  
25 from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred nonionic surfactants are of the formula R<sup>1</sup>(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH, wherein R<sup>1</sup> is a C<sub>10</sub>-C<sub>16</sub> alkyl group or a C<sub>8</sub>-C<sub>12</sub> alkyl phenyl group, and n is from 3 to about 80.  
30 Particularly preferred are condensation products of C<sub>12</sub>-C<sub>15</sub> alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C<sub>12</sub>-C<sub>13</sub> alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula



wherein R is a C<sub>9-17</sub> alkyl or alkenyl, R<sub>1</sub> is a methyl group and Z is glyceryl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent No. 2,965,576 and  
5 Schwartz, U.S. Patent No. 2,703,798, the disclosures of which are incorporated herein by reference.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18  
10 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Cationic surfactants can also be included in the present invention. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical. Pentavalent nitrogen ring compounds are also considered quaternary nitrogen compounds. Suitable anions are halides, methyl sulfate and hydroxide. Tertiary amines  
15 can have characteristics similar to cationic surfactants at washing solution pH values less than about 8.5. A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Cationic surfactants are often used in detergent compositions to provide fabric  
25 softening and/or antistatic benefits. Antistatic agents which provide some softening benefit and which are preferred herein are the quaternary ammonium salts described in U.S. Patent 3,936,537, Baskerville, Jr. et al., issued February 3, 1976, the disclosure of which is incorporated herein by reference.

#### Detergency Builder

The present process includes the step of inputting a detergent builder into the high speed mixer/densifier to coagglomerate with the surfactant paste. The builder also assists in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal of particulate soils from surfaces. Builders can operate via a variety of mechanisms including forming soluble or insoluble complexes with hardness ions, by ion  
35 exchange, and by offering a surface more favorable to the precipitation of hardness ions than are the surfaces of articles to be cleaned. Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at



least about 1% builder. Liquid formulations typically comprise about 5% to about 50%, more typically 5% to 35% of builder. Granular formulations typically comprise from about 10% to about 80%, more typically 15% to 50% builder by weight of the detergent composition. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; silicates including water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as well as amorphous-solid or non-structured-liquid types; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; aluminosilicates; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein. In terms of relative quantities of surfactant and builder in the present detergents, preferred builder systems are typically formulated at a weight ratio of surfactant to builder of from about 60:1 to about 1:80. Certain preferred laundry detergents have said ratio in the range 0.90:1.0 to 4.0:1.0, more preferably from 0.95:1.0 to 3.0:1.0.

P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

Suitable silicate builders include alkali metal silicates, particularly those liquids and solids having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1, including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL<sup>®</sup>, e.g., BRITESIL H<sub>2</sub>O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. NaSKS-6, sometimes abbreviated "SKS-6", is a crystalline layered aluminum-free  $\delta\text{-Na}_2\text{SiO}_5$  morphology silicate marketed by Hoechst and is preferred especially in granular laundry compositions. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043. Other layered silicates, such as

those having the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0, can also or alternately be used herein. Layered silicates from Hoechst also include NaSKS-5, NaSKS-7 and NaSKS-11, as the  $\alpha$ ,  $\beta$  and  $\gamma$  layer-silicate forms. Other silicates may also be useful, such as magnesium silicate, which can serve as a crispening agent in granules, as a stabilizing agent for bleaches, and as a component of suds control systems.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following general formula in an anhydride form:  $x\text{M}_2\text{O} \cdot y\text{SiO}_2 \cdot z\text{M}'\text{O}$  wherein M is Na and/or K, M' is Ca and/or Mg; y/x is 0.5 to 2.0 and z/x is 0.005 to 1.0 as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973, although sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, and other carbonate minerals such as trona or any convenient multiple salts of sodium carbonate and calcium carbonate such as those having the composition  $2\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3$  when anhydrous, and even calcium carbonates including calcite, aragonite and vaterite, especially forms having high surface areas relative to compact calcite may be useful, for example as seeds or for use in synthetic detergent bars.

Aluminosilicate builders are especially useful in granular detergents, but can also be incorporated in liquids, pastes or gels. Suitable for the present purposes are those having empirical formula:  $[\text{M}_z(\text{AlO}_2)_z(\text{SiO}_2)_v] \cdot x\text{H}_2\text{O}$  wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP. Natural types, including clinoptilolite, may be used. Zeolite A has the formula:  $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$  wherein x is from 20 to 30, especially 27. Dehydrated zeolites ( $x = 0 - 10$ ) may also be used. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether

polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 5 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid 10 and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrates, e.g., citric acid and soluble salts thereof are important carboxylate builders e.g., for heavy duty liquid detergents, due to availability from renewable resources and biodegradability. Citrates can also be used in granular compositions, especially in 15 combination with zeolite and/or layered silicates. Oxydisuccinates are also especially useful in such compositions and combinations.

Where permitted, and especially in the formulation of bars used for hand-laundering operations, alkali metal phosphates such as sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as 20 ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates, e.g., those of U.S. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137 can also be used and may have desirable antiscaling properties.

Certain deterative surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant 25 capability, these materials are summed up as deterative surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2- 30 dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide 35 additional builder activity. Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

Optionally, inorganic builder materials can be used which have the formula  $(M_x)_i Ca_y (CO_3)_z$  wherein  $x$  and  $i$  are integers from 1 to 15,  $y$  is an integer from 1 to 10,  $z$  is an integer from 2 to 25,  $M_i$  are cations, at least one of which is a water-soluble, and the equation  $\sum_i = 1-15(x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$  is satisfied such that the formula has a neutral or "balanced" charge. Waters of hydration or anions other than carbonate may be added provided that the overall charge is balanced or neutral. The charge or valence effects of such anions should be added to the right side of the above equation. Preferably, there is present a water-soluble cation selected from the group consisting of hydrogen, water-soluble metals, hydrogen, boron, ammonium, silicon, and mixtures thereof, more preferably, sodium, potassium, hydrogen, lithium, ammonium and mixtures thereof, sodium and potassium being highly preferred. Nonlimiting examples of noncarbonate anions include those selected from the group consisting of chloride, sulfate, fluoride, oxygen, hydroxide, silicon dioxide, chromate, nitrate, borate and mixtures thereof. Preferred builders of this type in their simplest forms are selected from the group consisting of  $Na_2Ca(CO_3)_2$ ,  $K_2Ca(CO_3)_2$ ,  $Na_2Ca_2(CO_3)_3$ ,  $NaKCa(CO_3)_2$ ,  $NaKCa_2(CO_3)_3$ ,  $K_2Ca_2(CO_3)_3$ , and combinations thereof. An especially preferred material for the builder described herein is  $Na_2Ca(CO_3)_2$  in any of its crystalline modifications. Suitable builders of the above-defined type are further illustrated by, and include, the natural or synthetic forms of any one or combinations of the following minerals: Afghanite, Andersonite, AshcroftineY, Beyerite, Borcarite, Burbankite, Butschliite, Cancrinite, Carboxenaite, Carletonite, Davyne, DonnayiteY, Fairchildite, Ferrisurite, Franzinite, Gaudefroyite, Gaylussite, Girvasite, Gregoryite, Jouravskite, KamphaugiteY, Kettnerite, Khanneshite, LepersonnateGd, Liottite, MckelveyiteY, Microsommite, Mroseite, Natrofairchildite, Nyerereite, RemonditeCe, Sacrofanite, Schrockingerite, Shortite, Surite, Tunisite, Tuscanite, Tyrolite, Vishnevite, and Zemkorite. Preferred mineral forms include Nyerereite, Fairchildite and Shortite.

#### Optional Detergent Components

The starting or entering detergent components in the present process can also include any-number of additional ingredients. These include other detergency builders, bleaches, bleach activators, suds boosters or suds suppressors, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference.

Bleaching agents and activators are described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983, and in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, both of which are incorporated herein by reference. Chelating agents are also described in

U.S. Patent 4,663,071, Bush et al., from Column 17, line 54 through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976 to Bartoletta et al., and 4,136,045, issued January 23, 1979 to Gault et al., both incorporated herein by reference.

5           Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

10           In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

**EXAMPLE**

This Example illustrates the process invention described and claimed herein. The percentages are on a weight basis, in the mixes prior to any subsequent follow-up drying, unless other wise specified. The terms "LAS" and "AS" as used herein mean, respectively, "sodium linear alkylbenzene sulfonate" and "sodium alkyl sulfate." Several surfactant pastes consisting of C<sub>14-15</sub>AS and C<sub>12,3</sub> LAS are made by sulfating C<sub>14-15</sub> alcohol with SO<sub>3</sub> and co-neutralizing with C<sub>12,3</sub>HLAS using 50% caustic soda (sodium hydroxide). The specific compositions of the surfactant pastes are set forth in Table I.

**Table I**

<b><u>Component</u></b>	<b><u>A</u></b>	<b><u>B</u></b>	<b><u>C</u></b>	<b><u>D</u></b>	<b><u>E</u></b>
C <sub>14-15</sub> alkyl sulfate	55.0	55.0	44.0	64.5	55.0
C <sub>12,3</sub> linear alkylbenzene sulfonate	18.3	18.3	29.3	8.8	18.3
Polyethylene Glycol 4000	3.7	3.7	3.7	3.7	0.0
Sodium Hydroxide	0.75	0.5	0.75	0.75	0.75
Water	19.5	19.5	19.5	19.5	23.2
Minors (sulfate, unreacted, etc.)	<u>2.75</u>	<u>3.0</u>	<u>2.75</u>	<u>2.75</u>	<u>2.75</u>
Total	100	100	100	100	100

- 10 A falling film SO<sub>3</sub> reactor is used to prepare the acid form of C<sub>14-15</sub> alkyl sulfate and C<sub>12,3</sub> linear alkylbenzene sulfonate. The acid is fed to a high active neutralization system which consists of a recycle loop containing a heat exchanger for cooling, a recirculation pump suitable for highly viscous fluids, and a high shear mixer with which the reactants are introduced. Surfactant paste exiting the high active neutralization system is transported and
- 15 stored in jacketed, temperature-controlled 316L stainless steel storage vessels at a temperature of 71°C. The surfactant paste remains stable and maintains a pH above 10 for at least five days (120 hours). The temperature of the paste is maintained between 65°C to about 70°C by the circulation of glycol solution through the vessel jacketing.

- Two feed streams of various detergent starting ingredients are continuously fed, at
- 20 a rate of 2800 kg/hr, into a Lödige CB-30 mixer/densifier, one of which comprises the surfactant paste and the other stream containing the detergent builder which is aluminosilicate. The surfactant paste, aluminosilicate and optional co-builder sodium carbonate are agglomerated to form detergent agglomerates. The detergent agglomerates from the Lödige CB-30 mixer/densifier are continuously fed into a Lödige KM-600
- 25 mixer/densifier for further agglomeration. The resulting detergent agglomerates are then fed to optional conditioning apparatus including a fluid bed dryer and a fluid bed cooler. The detergent agglomerates exiting the fluid bed cooler are screened, after which adjunct detergent ingredients are admixed therewith to result in a fully formulated detergent product having a uniform particle size distribution.

The composition of the detergent agglomerates exiting the fluid bed cooler is set forth in Table II below:

**Table II**

<u>Component</u>	<u>% Weight</u>
C <sub>14-15</sub> alkyl sulfate and C <sub>12,3</sub> linear alkylbenzene sulfonate	30.0
Aluminosilicate	36.0
Sodium Carbonate	21.0
Misc. (water, perfume, etc.)	<u>13.0</u>
Total	100.0

- Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.
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## WHAT IS CLAIMED IS:

1. A process for preparing detergent agglomerates characterized by the steps of:
  - (a) providing a non-linear viscoelastic surfactant paste including, by weight of said surfactant paste, from 70% to 95% of a deterative surfactant, from 5% to 30% of water, and an excess amount of an alkali metal hydroxide such that the pH of said surfactant paste is at least 10;
  - (b) regulating the temperature of said surfactant paste within a range from 50°C to 80°C so that said surfactant paste is processable and stable for at least 48 hours;
  - (c) charging said surfactant paste into a high speed mixer/densifier;
  - (d) inputting from 1% to 70% by weight of a detergency builder into said high speed mixer/densifier; and
  - (e) agglomerating said surfactant paste and said builder by treating said surfactant paste and said builder initially in said high speed mixer/densifier and subsequently in a moderate speed mixer/densifier so as to form said detergent agglomerates.
2. The process according to claim 1 wherein said surfactant paste is substantially free of materials which produces a gas when reacted with an acid.
3. The process according to claims 1-2 wherein said alkali metal hydroxide in said surfactant paste is sodium hydroxide.
4. The process according to claims 1-3 wherein said deterative surfactant is a mixture of alkyl sulfate and linear alkylbenzene sulfonate surfactants in a weight ratio of from 1:1 to 5:1.
5. The process according to claims 1-4 further characterized by the step of drying said detergent agglomerates.
6. The process according to claims 1-5 wherein said detergency builder is aluminosilicate.
7. The process according to claims 1-6 wherein said regulating step renders said surfactant paste stable for at least 72 hours.





## DECLARATION COMBINED WITH POWER OF ATTORNEY

Page 1 of 2

Attorney Docket No. 6065

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **HIGH DENSITY DETERGENT-MAKING PROCESS USING A HIGH ACTIVE SURFACTANT PASTE HAVING IMPROVED STABILITY** the specification of which

(check ☐ is attached hereto.  
one) ☒ was filed on April 16, 1997 as  
Application Serial No. PCT/US 97/06484  
and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37 Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35 United States Code §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)Priority Claimed

(Number)

(Country)

(Day/Month/Year Filed)

☐  
Yes☐  
No

(Number)

(Country)

(Day/Month/Year Filed)

☐  
Yes☐  
No

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

60/015,685April 17, 1996

Application Serial No.

Filing Date

Application Serial No.

Filing Date

I hereby claim the benefit under Title 35 United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

I hereby appoint the following as my attorney(s) or agent(s) with full power of substitution to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Associate Power

of Attorney Attached

☐ Yes ☒ No

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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